

KINETICS OF THE HETEROPHASE POLYMERIZATION OF VINYL ACETATE IN THE PRESENCE OF A LIMITED AMOUNT OF AN ANIONIC SURFACTANT

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Vinyl acetate (VAc) was polymerized in an aqueous system with a limited concentration (0.32%) of the anionic surfactant sodium dodecyl sulfate (SDS). The surfactant concentration was slightly above the critical micelle concentration. Initially, the micellar solution and the initiator were charged into the reactor. Then, batch polymerization was started with 1.5% VAc at 60° C. After 30 minutes of reaction more VAc was added in a semicontinuous manner. The addition was continued until the total polymer concentration was 12%. The rate of polymerization showed three regions: (I) particle nucleation, (II) constant rate and (III) decreasing rate periods. The increase of the polymer particles surface area (A_i) was analyzed as a function of reaction time. It was found that, by the time when the micelles have been consumed the total polymer particles surface area was higher than the area that the surfactant molecules could cover long before the end of the reaction. However, the number of particles remained approximately constant during the polymerization. Particle diameter increased continuously up to 45 nm by the end of the polymerization. The results indicate that the particle growth was due to the continuous conversion of monomer to polymer during polymerization and not to particle coagulation.

Introduction

Microemulsion homopolymerization of unsaturated monomers has been intensively investigated during the past 25 years. Particularly in the latest years, the reports on this polymerization process has been continuously increasing.¹ Even though the emulsion polymerization of vinyl acetate (VAc) has been extensively reviewed² there is a lack of published work about the polymerization of this monomer by microemulsion processes. It is well known that, although there are some similarities between the two processes they have important differences from the kinetics point of view. For instance, emulsion polymerization exhibits three reaction rate intervals whereas only two are detected in microemulsion polymerization.³ Additionally, the molar mass obtained by microemulsion polymerization of VAc is smaller than the one observed in emulsion polymerization.³⁻⁵

Until now, the principal aspects investigated about the microemulsion homopolymerization of VAc have been focused principally on: the effects of monomer concentration, initiator concentration and the kind of initiator employed on the molar weight and on the rate of polymerization.³⁻⁵ Furthermore, it has been developed a method to obtain latexes with high solids content.⁶

Although the latex made by microemulsion polymerization have some interesting advantages over the ones made by emulsion polymerization, from the point of view of the industrial applications, the large amounts of surfactants required for the formulation limits its scale up to industrial level.⁷ Only Sosa and col. have polymerized under conditions where the surfactant concentrations were close to 1%.^{3,6}

The purpose of the present work is to report a study of the polymerization of VAc under conditions where the surfactant concentration was slightly above the critical micelle concentration, 0.32% with respect to the water used in the formulation.

Experimental

Distilled and deionized water was employed. All reactants (purity>98.5%) were purchased from Aldrich. VAc was purified via liquid-liquid extraction according to the procedure reported by Perrin and Amarego⁸ for ethyl acrylate. Finally the monomer was kept under refrigeration. The other reactants were used as received.

The partial phase diagram of the ternary system VAc/H₂O/SDS was built up titrating aqueous solutions of SDS with VAc at 60°C in sealed bottles. VAc was added drop to drop to the bottles until saturate the solution. This point was easily recognized because the solution turned lightly cloudy. When it was raised we stop the VAc addition and the composition of the system was taken like the limit between microemulsion and emulsion region. The partial phase diagram obtained whit that procedure agreed with the one published by Donescu and col.⁹

The polymerizations were carried out at 60 °C in a 500-mL glass jacketed reactor with three inlets. The reaction mixture was stirred mechanically at 330 rpm. The polymerization was started as a batch pre-polymerization stage and was followed by a semicontinuous polymerization stage. The initial reaction mixture composition for the pre-polymerization was selected from the constructed partial phase diagram in the low surfactant water-rich oil-in-water microemulsion region. The surfactant concentration was slightly above the critical micelle concentration. At the beginning, the micellar solution and the initiator (KPS, 2% with respect to the monomer) were charged into the reactor. Then, the reaction mixture temperature was increased to 60° C and the batch polymerization was started with a one-shot addition of 1.5% VAc. After 30 minutes of reaction (approximately, 35% conversion) more VAc was added in a semicontinuous manner at a rate to maintain monomer starved conditions in the reaction mixture. At the same time, an extra addition of KPS (0.3 g in aqueous solution) was poured into the reactor in a single shot. The addition of VAc was continued until the total polymer concentration was 12% and the reaction mixture was kept under agitation for an additional hour. VAc monomer was oxygen-free and a stream of ultrahigh purity nitrogen was continuously bubbled into the reaction mixture during the whole polymerization process. Samples were taken from the reactor at specific times for conversion determination by gravimetry. The streams into and out of the reactor were controlled in order to perform material balances.

Particle size was determined by quasi-elastic light scattering with a Nano S90 (Malvern) at 25° C using the water viscosity as that of the sample. The latex was diluted up to 1000 times with an SDS solution before the measurements to minimize particle-particle interactions.

Results and Discussion

Figure 1 shows the partial phase diagram of the ternary system VAc/H₂O/SDS, in which the red point marks the composition of the initial reaction mixture as well as illustrates the really low surfactant concentration employed in our formulation.

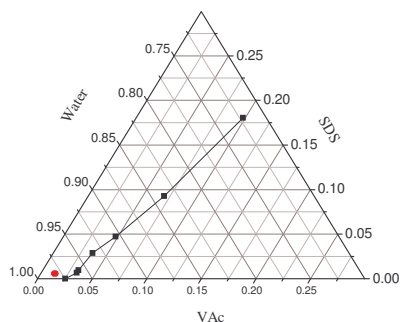


Figure 1. Partial phase diagram for the ternary system VAc/H₂O at 60 °C. The red rounded point represents the composition of the initial reaction mixture.

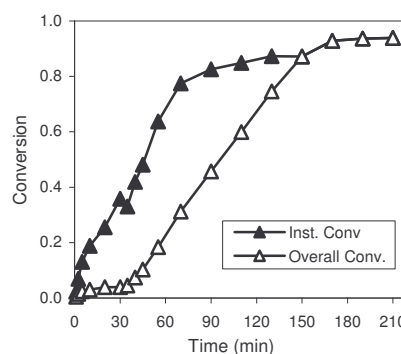


Figure 2. Instantaneous and overall conversion for the pre-polymerization and semicontinuous period.

Figure 2 depicts the instantaneous and the overall conversion. Instantaneous conversion at time t was referred to the total monomer fed up to that time, overall conversion was referred to the total monomer fed to the reactor at the end of the polymerization. It can be seen that the first thirty minutes describe the pre-polymerization period. From this point on the semicontinuous polymerization starts with the addition of more VAc at an addition rate of ~ 0.37 g/min for two hours. At the same time, 0.3 g of KPS in aqueous solution were added in one shot. It can be observed from the instantaneous conversion curve that after a period of continuous feeding the instantaneous conversion approaches a steady state. This has been observed for the semicontinuous polymerization of several monomers.⁸ At the end of polymerization, the total conversion was $\sim 96\%$ and the polymer content in the latex was $\sim 12\%$ which was very high for the low surfactant content.

Figure 3 shows the polymerization rate curve and the evolution of average particle number (N_p) with time. It can be seen that the polymerization rate presents three well defined periods of polymerization (I) particle nucleation, in which the rate of polymerization increases; (II) constant rate and (III) decreasing rate periods.

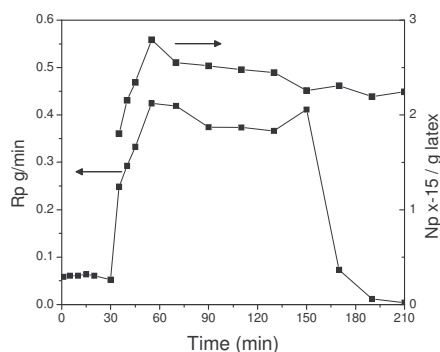


Figure 3. Rate of polymerization and evolution of the average number particles.

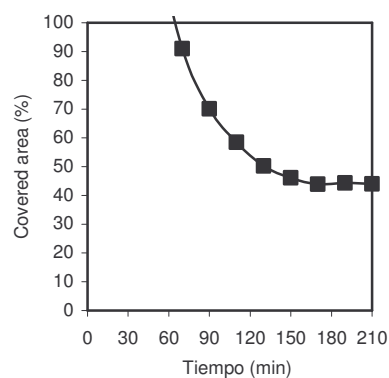


Figure 4. Experimental surface area of polymer particles covered by the surfactant.

The first thirty minutes of the curve represent the rate of polymerization of the pre-period. As can be noticed, the rate of polymerization in this period is very low and, consequently conversion is low too (Figure 2). When the semicontinuous polymerization starts the rate increase rapidly and the period of particle nucleation (I) continues approximately twenty five minutes more. While this process is active N_p is continuously increasing. At the end of this period, N_p decrease slightly up to the end of the monomer addition. However, polymerization rate remains approximately constant (II), maybe this behavior is originated in part because there is a balance into the polymer particles between the monomer concentration and the radical concentration. The period of constant polymerization rate (II) finished when the semicontinuous monomer addition was stopped and from this time on, the polymerization rate began to decrease continuously until the end of the reaction. It is important to comment that the addition rate of monomer to the reaction system is close to the maximum polymerization rate, consequently, we can assert that the polymerization was performed at monomer starved conditions.

The experimentally calculated average surface area covered by the surfactant used in the formulation of the reaction assuming that all the surfactant employed in the formulation is absorbed at the polymer particle-water interface is shown in Figure 4. It can be seen from the curve that initially the area covered by the surfactant decreases very fast with reaction time (see also we Figure 3). This fact occurs by the time when the micelles had been consumed (onset of period II). The marked decrease in the covered area caused that the total polymer particles surface area was higher than the area that the surfactant molecules could cover long before the end of the reaction. Nevertheless, despite of the low surfactant content, N_p remained approximately constant in period II (Figure 3) and the particles were relatively stable to coagulation during the polymerization. Figure 5 shows the evolution of the average particle diameters with the time of reaction. This figure shows a continuous increment in the average particle diameter and, to some extent, its behavior reflects the three periods of the rate of polymerization; that is, each period causes different behavior in the growth of the polymer particles.

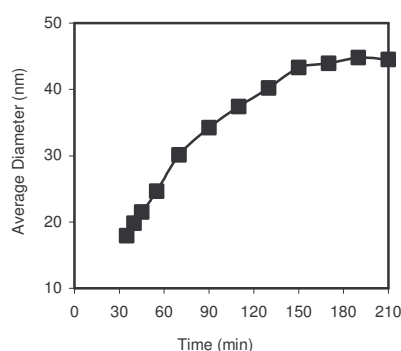


Figure 5. Experimental average particle diameters.

Based in the relatively constant N_p we can suppose that the continuous increment in average polymer particle size with the polymerization time was due principally to the continuous conversion of monomer to polymer into the particles and not to a particle coagulation process. The particle size reached at the end of the polymerization was ~ 45

nm, and although the polymer content was 12%, the latex obtained had all the features of the microemulsion made latexes. An important result, was that the efficiency in the production of polymer content in the latex to the surfactant employed was 37.5, which is very high for microemulsion polymerizations.

Conclusions

For the microemulsion polymerization, despite of the limited surfactant content used in the formulation, it was possible to achieve high efficiency in the production of the polymer content in the latex to the surfactant employed (37.5), with high conversion (~96%) at the end of the reaction. The rate of polymerization showed three well – defined regions: (I) particle nucleation, in which the rate of polymerization increases; (II) constant rate and (III) decreasing rate periods. These periods agree with the protocol carried out for the reaction. When the micelles had been consumed at the beginning of period II, the surface area of the polymer particles covered by the surfactant decreased dramatically, however, the average particle number did not suffer a notable change while the reaction was performed. This observation can be taken as an indication of good colloidal stability of the dispersed particles with respect to coagulation.

References

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